AD-A258 034

QUARTERLY REPORT FOR ALE PROJECT
OCTOBER 1992

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Contract # N00014-91-C-0080

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The key areas of progress in this reporting period are outlined below:

1. Self limiting Surface reactions

- Surface chemistry involved in the chemisorption and decomposition of diethylsilane on Silicon:

An abundance of silicon and germanium hydrides, halides and halohydrides exist as possible precursors for group IV atomic layer epitaxy (ALE). So far these have been the main focus of investigations. Recently, alkylsilanes and alkylgermanes have been considered as possible candidates for silicon and germanium ALE by Coon et al. These chemicals belong to an advantageous subset of all possible molecular candidates, because they are less toxic and flammable than silicon and germanium hydrides and halohydrides. However, an inherent potential problem needs to be investigated for such an application, namely, the codeposition of carbon on the semiconductor surface. On the other hand, such a potential drawback may be put to good use for growing epitaxial $Si_{1-y}C_y$ films.

We have probed the surface chemistry involved in the chemisorption and thermal reaction of diethylsilane (DES) on Si(111) and Si(100), for growth at room temperature and subsequent annealing as well as for growth at elevated temperature. As fingerprints of the chemical state of the surface species we have used surface-sensitive photoelectron spectroscopy with synchrotron radiation, probing the valence band, the shallow C2s core level, and the C1s and Si2p core levels. Ethyl groups at the surface are identified by two sharp peaks at 14.3 and 17.9 eV below the Fermi level representing the bonding and antibonding combinations of the C2s levels of the two C atoms (see Figure 1). For alkyl groups in general, the number of C2s components observed in the valence band spectrum is directly related to the number of C atoms in the hydrocarbon chain. We find that DES chemisorbs dissociatively to form $Si - CH_2CH_3$ surface species on Si(111) and (100) at room temperature. Anneals of the (111) and (100) surfaces to temperatures of 300 and 350 C, respectively, promote the onset of desorption of the ethyl groups from the surface. Although decreasing in intensity they continue to persist until a temperature of 400 and 550 C is attained for Si (111) and (100), respectively. At these temperatures, the remaining ethyl species dissociate to form Si-C surface species. For growth at elevated temperature we find that carbon is codeposited with silicon from DES.

- Growth of thin Si films on Ge(100) substrates using alternating exposure to Si_2Cl_6 and Si_2H_6

As shown in Appendix A, thin Si films have been grown isothermally on Ge(100) substrates using alternating exposures of Si_2H_6 and Si_2Cl_6, maintaining chlorine and hydrogen surface termination. At 465°C, film growth rate is roughly 2 monolayer per cycle (one cycle equals 1 Si_2H_6 and 1 Si_2Cl_6 exposure). The Cl + H adlayer acts as a surfactant, enabling a uniform epitaxial film to be grown at 475°C. Islanding of the Si, and 3-d growth, is observed at higher T (510°C). This process is thermally activated and is not strictly self-limiting, but has certain desirable characteristics of atomic layer epitaxy growth.

- A real time *in situ* study of the adsorption of the precursors $SiClH_3$ and $SiCl_2H_2$ on Si(100) at 450-550°C, which demonstrates that $SiCl_2H_2$ adsorption is not self-limiting at T > 500°C.

Appendix B reports on the adsorption of $SiClH_3$ and $SiCl_2H_2$ on Si(100), studied as a function of temperature using real time *in situ* methods. The objective is to compare these precursors for Si Atomic Layer Epitaxy (ALE). At 450-550°C, a substantial surface H coverage (θ_H) exists during $SiClH_3$ adsorption, and θ_H exhibits transient behavior. During $SiCl_2H_2$ adsorption, θ_H is much smaller. At 500°C with $SiCl_2H_2$, $\simeq$ 1 monolayer of Cl is formed after $\simeq 4 \times 10^{19}$ cm^{-2} exposure. Dichlorosilane is a suitable precursor for Si ALE, but desorption of HCl is significant at T > 500°C so that $SiCl_2H_2$ adsorption is not strictly self-limiting.

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- A comparison of Si ALE chemistries based on equilibrium thermodynamics:

   Appendix C reports a comparison of thermodynamics of various chemical schemes for Si Atomic Layer Epitaxy (ALE). These are analyzed using a 2-step sequence of reactions : 1. surface chlorination , using a chlorosilane molecule, and 2. reduction (Cl removal) using atomic H or a silane molecule. The schemes were compared in terms of equilibrium thermodynamics, to select the most promising schemes. All of the proposed processes based on atomic H are spontaneous (thermodynamically downhill). Two reactions using Si_2H_6 are endothermic, but may be thermally driven at useful Si growth temperatures, due to a large, positive entropy change for the reaction.

2. Growth Studies

In the past we focussed on the use of atomic layer epitaxy (ALE) like processes for the p- and n-type doping of Si by atmospheric pressure CVD. In the last quarter we tried to apply this technique to the implementation of Ge and SiGe layers into Si. The basic principle of the technique explored is the exposure of a Si surface to a reactive gas at low temperatures to obtain a monolayer coverage. The growth temperature is than slowly raised again and the layer is covered with Si in a standard non-ALE process.

At first we investigated the growth rate of Ge on Si in dependence of the temperature. Fig. 2 shows the growth rate on a logarithmic scale in dependence of the reciprocal growth temperature. The growth rate for Ge on Si using GeH_4 as the reactive gas in a H_2 carrier is nearly independent of the growth temperature, revealing rather high growth rates at temperatures as low as 400°C. (dashed curve in Fig. 2) No self-limiting process for the chemisorbtion of Ge is found. A stronger dependence for the Ge growth rate is found when $SiCl_2H_2$ (DCS) is added to grow SiGe. In this case the growth rate for Si is increased compared to the rate observed from DCS alone (dotted curve) and the rate for Ge decreases at low temperatures compared to the dashed curve. This indicates rather complex gas phase and surface kinetically reactions in the APCVD process, which need further investigation to achieve an understanding of the detailed mechanisms. However, the presence of chlorine compounds shifts the Ge growth rate from the more diffusion controlled growth regime to a kinetically controlled process. The latter is essential for an ALE process.

Even though no self-limitation is found yet, the small growth rate for SiGe allows an excellent control of the SiGe layer width by the proposed technique. Fig. 3 shows to photoluminescence spectra of SiGe/Si multiple quantum well (MQW) structures grown with the following growth sequence. The growth of Si was interrupted and the surface was exposed for a time t_E to DCS and GeH_4. After the exposure the reactor was purged with H_2 and then the growth of Si was resumed. In sample (a) t_E was 4 s and in sample (b) 5 s. The PL spectra reveal excitonic spectra with resolved no-phonon lines and several phonon assisted recombination lines. Each spectrum has two no-phonon lines at energies of 1065.7 and 1082 mev for sample (a) and 1053 and 1064.9 meV in sample (b). The spectra have a common no-phonon line at 1065 meV. The line at 1082 meV is attributed to areas within the MQW which are one monolayer thinner and the line 1053 mev to areas which are one monolayer thicker than areas leading to the line at 1065 meV. In consequence the average thickness of the SiGe quantum wells is 1-2 monolayers larger in sample (b) than in sample (a). In addition, the data indicate within the samples a layer to layer reproducibility of one monolayer. The narrow line widths also indicate a reproducibility of the Ge fraction within the MQW of less than 0.5%. We therefore conclude that we achieved monolayer control for SiGe layers by this ALE-like epitaxial process.
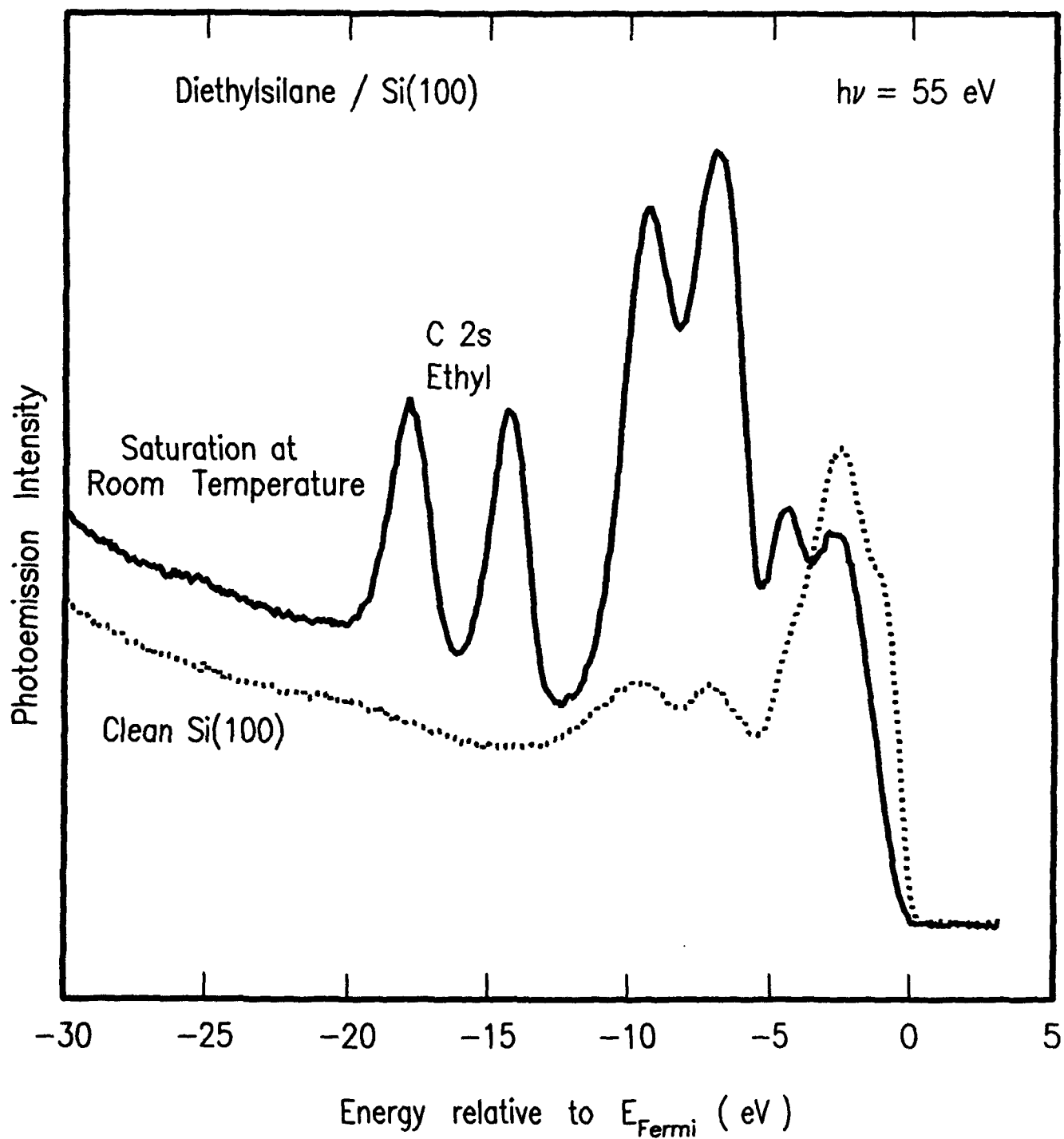
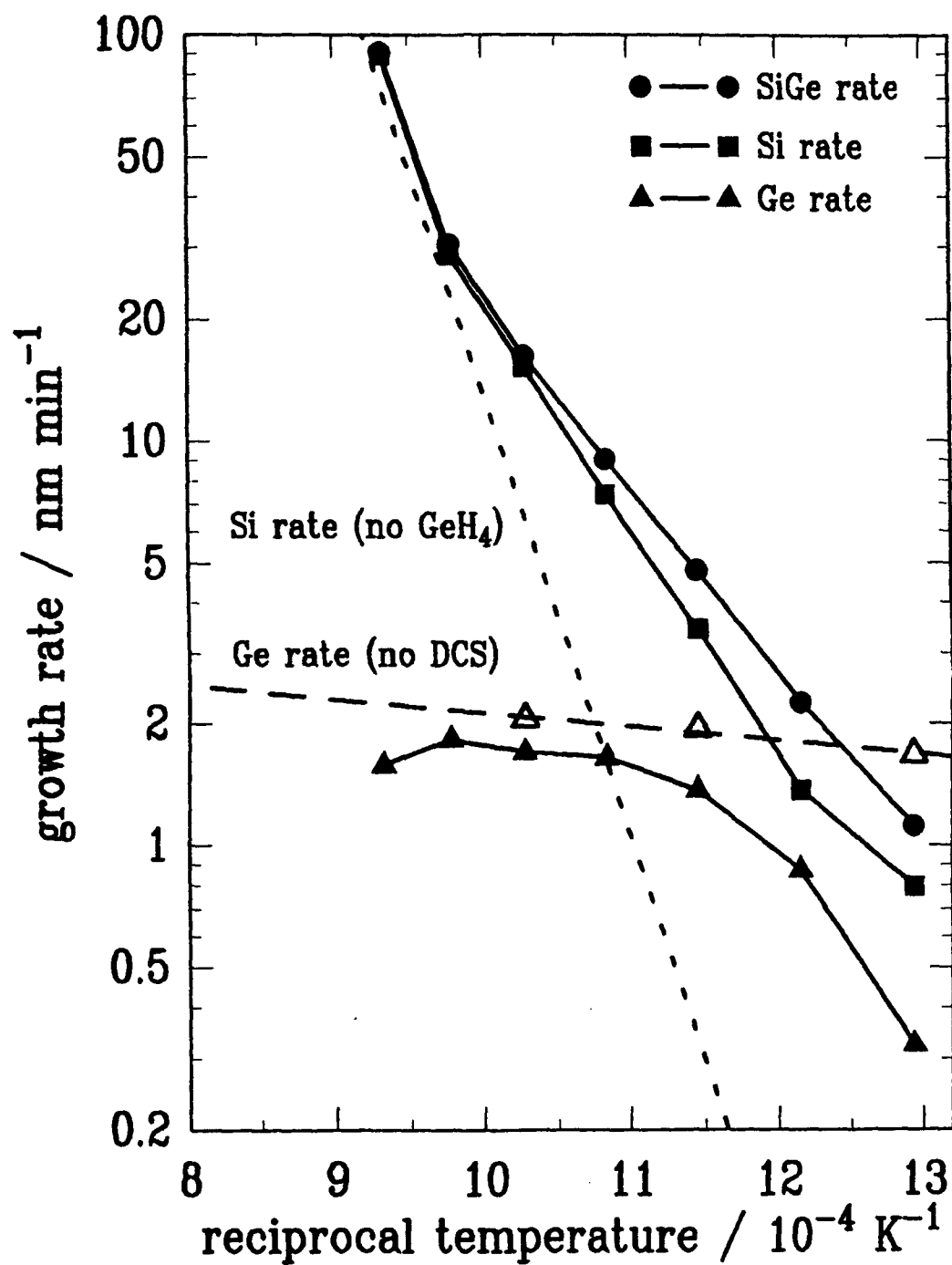Figure 1. Core level spectra showing (a) Clean silicon and (b) Silicon saturated with DES

Figure 2. Growth rates for Ge on Si(100)

EPITAXIAL Si FILMS ON Ge(100) GROWN VIA H/Cl EXCHANGE

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ABSTRACT

Thin Si films have been grown isothermally on Ge(100) substrates using alternating exposures of Si_2H_6 and Si_2Cl_6, maintaining chlorine and hydrogen surface termination. At 465°C, film growth rate is roughly 2 monolayer per cycle (one cycle equals 1 Si_2H_6 and 1 Si_2Cl_6 exposure). At 475°C a uniform epitaxial film is obtained, while islanding is observed at higher T. This process is thermally activated and is not strictly self-limiting, but has certain desirable characterisitics of atomic layer epitaxy growth.

PACS numbers : 68.55.Ln , 68.35.Dv , 81.15.Gh , 82.65.Yh

The primary advantage seen in growth of Si and SiGe alloys via the layer-by-layer growth method known as Atomic Layer Epitaxy (ALE) [1,2] is fine control over deposited layer thickness. Approaches to ALE of Si have included pulsed laser heating [3], synchrotron radiation [4], or high temperature (T) [5] to regenerate a bare, dangling bond (db) terminated, Si surface following saturation exposure to Si_2H_6 [3] or $SiCl_2H_2$ [4,5]. We report here on the first low temperature, isothermal, growth of thin epitaxial Si films using ALE chemistry, specifically alternating exposures of Si_2Cl_6 and Si_2H_6. Rather than regenerate a db-terminated surface, this method maintains surface termination with a mixed Cl + H adlayer. The adlayer acts as a surfactant [6], resulting in continuous, highly uniform, Si films grown below 500°C.

Here, each growth cycle consists of separate exposure to Si_2H_6 and Si_2Cl_6. An initial Si_2H_6 exposure largely covers the Ge(100) surface with Si. Thereafter, Si_2Cl_6 is dosed onto the H-terminated surface (30 s at 0.002 torr), and Si_2H_6 is dosed onto the Cl-terminated surface (300 s at 0.005 torr). Using surface sensitive direct recoiling (DR) analysis, the exposures of Si_2H_6 and Si_2Cl_6 required to complete the exchange reactions have been reported as a function of T on Si(100) [7], but film crystallinity and morphology were not studied. At 515°C and below, the chlorination step is self-limiting. The Cl removal step using Si_2H_6 appears to be kinetically controlled [7] and is not self-limiting. We designate these films as Si*. We show here that the Si* thickness is a linear function of the number of growth cycles, and the growth rate is $\simeq 2$ monolayer (ML)/cycle at 465°C. 1 ML equals 6.8×10^{14} Si atoms cm^{-2}.

The Si on Ge epitaxy system has remained relatively unexplored compared to Ge on Si. Heteroepitaxy has been investigated for Si on Ge(100) using electron spectroscopies [8] and Si on Ge(111) using medium energy ion scattering (MEIS) [9]. In the absence of surfactants, the normal growth mode is island formation (Volmer-Weber) [8,9]. Copel and co-workers have utilized As as a surfactant in the growth of Si on a thin Ge

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layer on Si(100), which changes the growth mode to uniform, layer by layer growth (Frank-Van der Merwe) {6}. Here, we report a dramatic effect of growth T on the Si* morphology in the range 465-515°C. Below 500°C, the surface remains terminated with Cl and/or H during growth, and this adlayer acts as a surfactant {6} giving uniform Si growth. This Cl+H adlayer may also inhibit Ge out-diffusion through the Si* film.

Thin Si films were grown isothermally in a (coldwall) stainless steel chamber (base pressure 2×10^{-9} torr) equipped with low energy electron diffraction (LEED) optics. The Ge(100) substrates were cleaned by 5 cycles of Ar^+ sputtering (5-10 minutes) and flashing to 750°C, followed by annealling at this T for 5 minutes. Good (2X1) LEED patterns were observed, and analysis by DR in a separate chamber showed the Ge(100) to be atomically clean after this procedure. *Ex situ* studies with cross-sectional transmission electron microscopy (XTEM) and MEIS were performed with a native oxide on the Si* films. Residual Cl in the films was < 0.1 atomic % as measured by secondary ion mass spectrometry.

Film morphology was studied by XTEM, with Si* grown for 20 growth cycles at 3 temperatures: 465, 475 and 515°C. Figure 1 shows XTEM micrographs from the 515°C (Top) and 475°C (Bottom) films. Common to both pictures are the (111) lattice fringes which propagate from the Ge(100) substrate into the Si*, confirming that the Si* is epitaxial. At 515°C, the film is characterized by few defects. However, the film is also highly non-uniform in thickness, consisting of large islands, apparently joined by a thin Si layer visible at the sides of the micrograph. Selected area diffraction from the Si islands further confirmed the epitaxial quality of the Si*. At 475°C, the Si film is continuous, very uniform in thickness (130 ± 10 Å), and contains an abundance of defects. Ge has a 4% larger lattice constant than Si, and the defects (dislocations and stacking faults) form in order to relieve strain in the Si* film. Homoepitaxy studies on

Si(100) are in progress aimed at establishing the defect density intrinsic to this process. A film grown at 465°C (XTEM not shown) exhibited uniform Si* thickness.

Information on Si* crystallinity, thickness and inter-diffusion with Ge was obtained from MEIS using a 200 keV He$^+$ beam. MEIS spectra for three samples grown at 465°C appear in Figure 2, with a solid line for the random incidence (x1) and shaded spectrum for the aligned (x5) geometries, respectively. The arrows at 191.6 keV indicate the energy for He$^+$ backscattering from a Ge surface layer. Such a layer might form by Ge out-diffusion to the Si* surface. Out-diffusion of Ge is negligible, giving < 1 atomic % Ge in the Si*, a result we confirmed by x-ray photoelectron spectroscopy. In the aligned spectra, all 3 of the films exhibit a Ge interface peak (187 to 183 keV) and a Si surface peak at $\simeq$ 178 keV. A Si interface peak develops in the thicker films (170-175 keV). Scattering intensity from within the Si* film in the aligned geometry is roughly 10% of that for the random incidence geometry, consistent with the presence of strain relief defects seen in Figure 1. (The aligned intensity is $\simeq$ 2 % for a high quality Si single crystal.)

Ions scattered from the Ge(100) interface lose energy during transit through the Si* overlayer, causing the Ge leading edge to shift below 191.6 keV in Figure 2. The shift was converted to thickness of Si* using tabulated values of the stopping power. The result, plotted in Figure 3, indicates that the Si* thickness correlates linearly to the number of growth cycles. This is a useful feature of the H/Cl exchange growth method. Independent evaluation by XTEM of the 15 cycle thickness agreed with the MEIS measurement within 2%. The solid line is a least squares fit to the data (slope = 1.95 ML/cycle, y-intercept = 7.2 ML). The non-zero y-intercept is considered below.

Elsewhere, we have speculated on the growth mechanism using Si_2H_6 and Si_2Cl_6 on the Si(100) surface {7}. *After* a continuous Si film is established on the Ge(100) surface,

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we speculate that $\simeq$ 1/3 ML of Si* is grown with each self-limiting Si_2Cl_6 exposure (1 ML of Cl as monochloride gives 2/6 ML of Si). During the Si_2H_6 exposure (300 s), Si* is probably grown via the desorption of *both* H_2 and HCl. The amount of Si* grown from Si_2H_6 is expected to be T dependent, and is $\simeq$ 1.6 ML at 465ºC.

We attribute the non-zero intercept in Figure 3 to fast initial growth of Si* during the first Si_2H_6 exposure, caused by the rapid desorption of H_2 from the Ge(100) surface. Si growth from Si_2H_6 on Si(100) is rate limited by H_2 desorption below $\simeq$ 550ºC {10,11}. The 1st order desorption rate for H_2 from Si(100) at 465ºC is $\simeq 10^{-2}$ s^{-1} {12}. On Ge(100), this rate is 10^4-10^5 faster {13}. Therefore, initial growth of Si* on Ge(100) should be significantly faster than similar growth on Si(100). Using DR analysis, we see nearly complete attenuation of the Ge DR signal after 1 growth cycle at 465ºC {14}.

We report here the first low T, isothermal, growth of epitaxial Si films using H/Cl exchange chemistry. Alternating exposures of Si_2H_6 and Si_2Cl_6 result in heteroepitaxy of Si on Ge(100) with a film thickness proportional to the number of growth cycles. Films grown below 500ºC are continuous and very homogeneous in thickness, but contain many strain relief defects.

Acknowledgements

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FIGURE CAPTIONS

FIGURE 1.Cross-section TEM micrographs of Si^* films on Ge(100), both taken at 550,000 magnification. Top panel: 20 cycles at 515ºC. Bottom panel: 20 cycles at 475ºC.

FIGURE 2. MEIS spectra from Si^* films on Ge(100) grown for the indicated number of cycles at 465ºC, using 200 keV He^+ ions. The He^+ beam is incident along a $(\bar{1}11)$ direction at 54.7º from the Ge(100) surface normal, and the detector is located at a 52.3º scattering angle. Solid Line : random incidence geometry, x1. Shaded Spectrum : aligned geometry, x5.

FIGURE 3. Solid points: thickness of Si^* film (derived from the MEIS data of Figure 2) plotted versus number of growth cycles. Solid line: least squares fit.
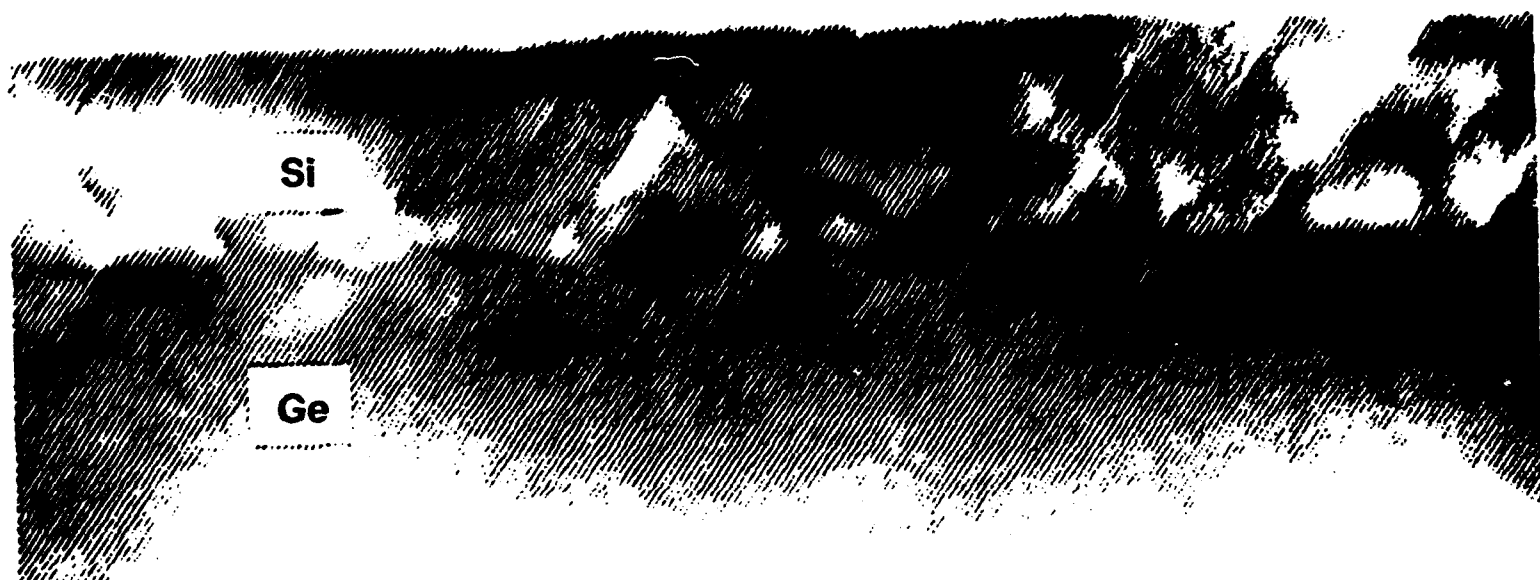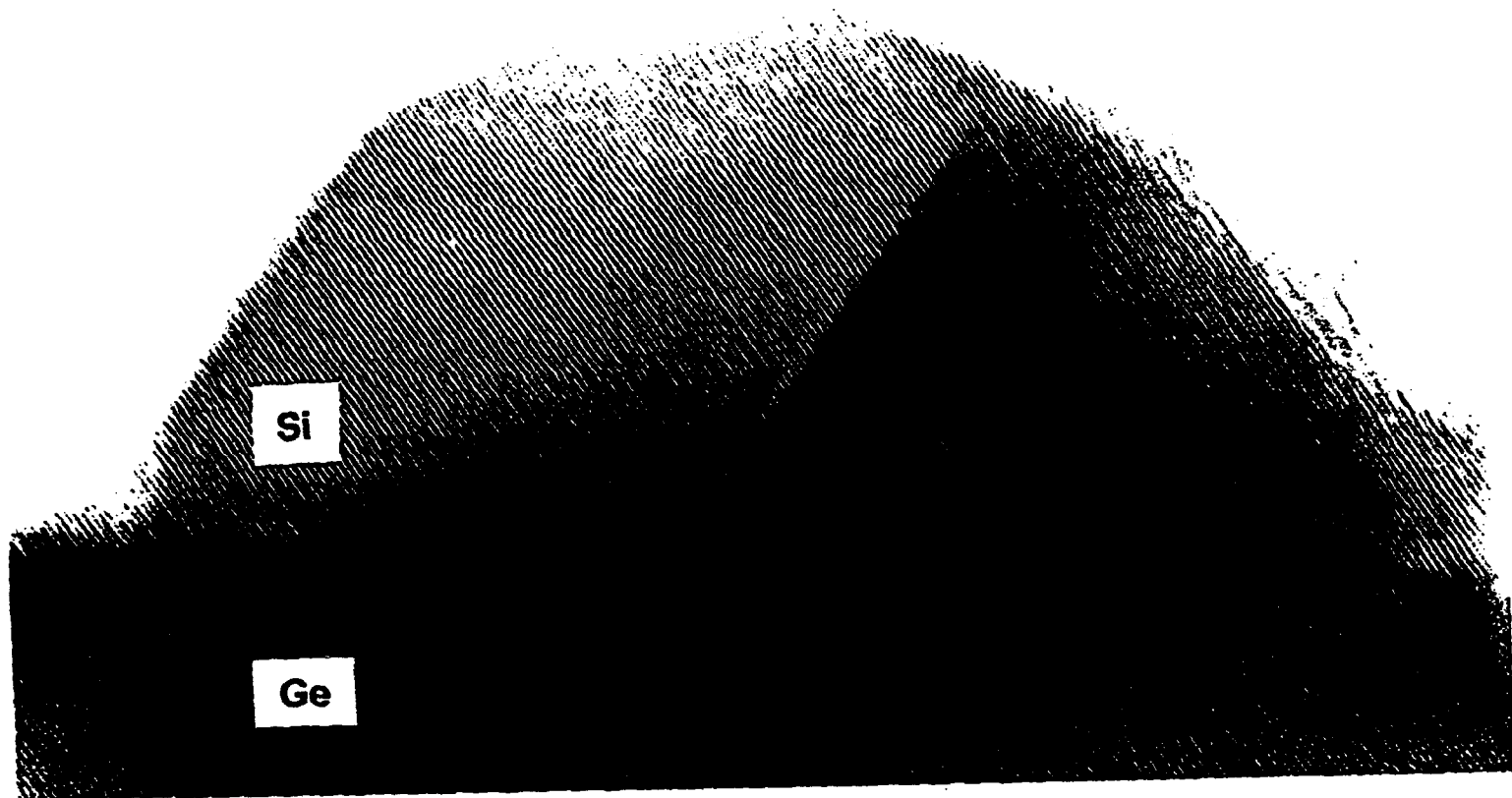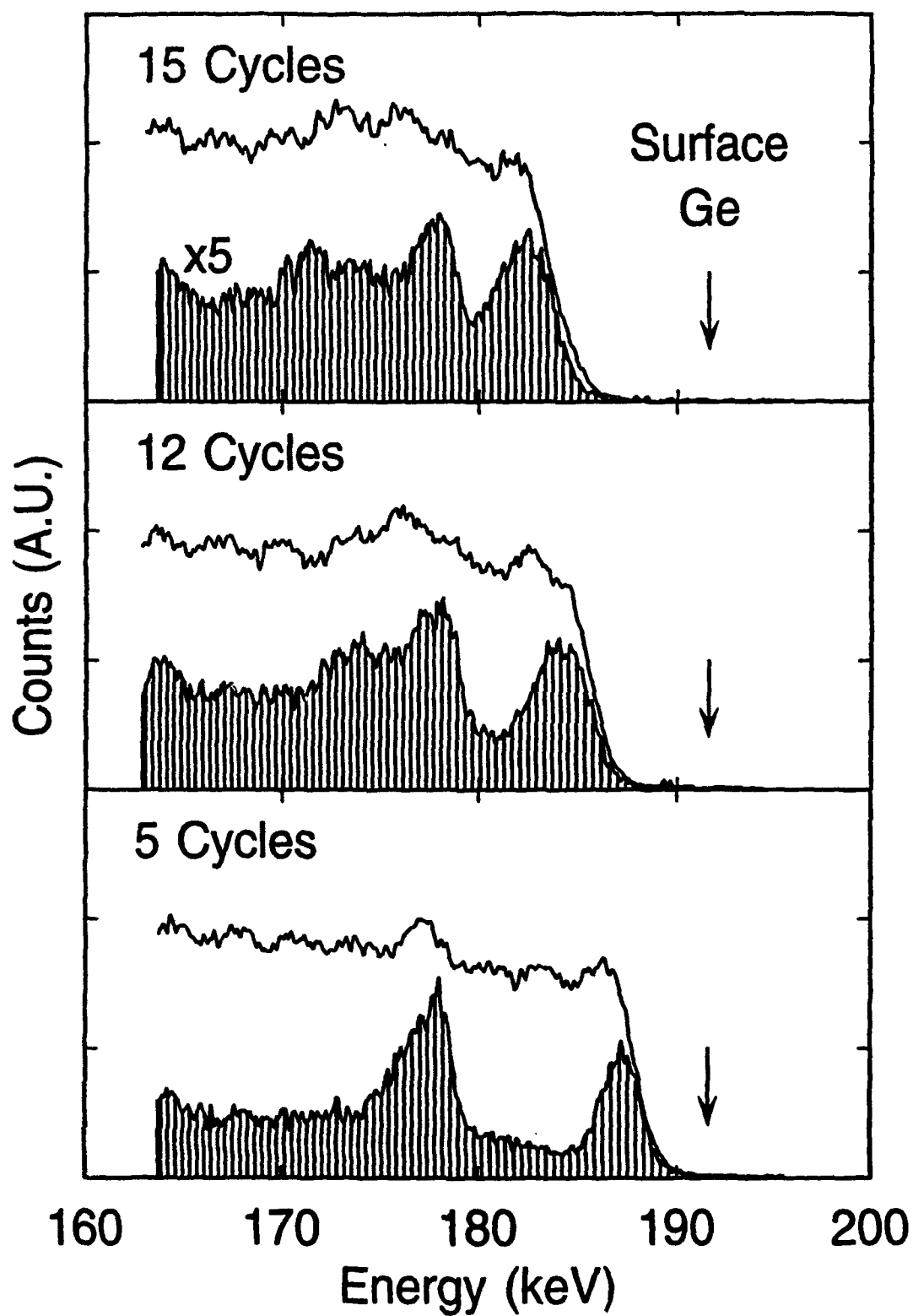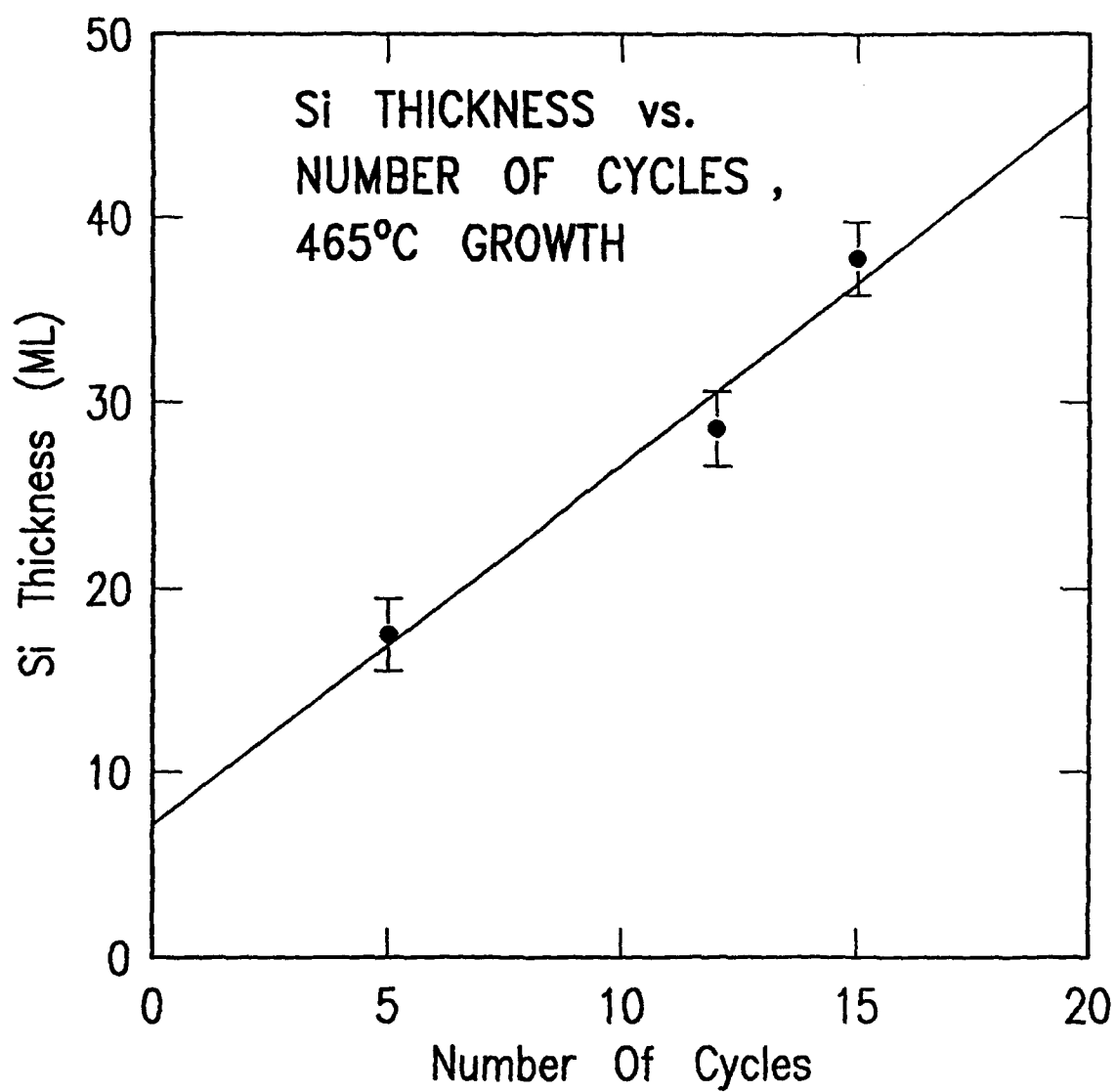
Fig. 1

Fig. 2

Fig. 5

Si THICKNESS vs. NUMBER OF CYCLES, 465°C GROWTH

PRECURSORS FOR Si ATOMIC LAYER EPITAXY:

REAL TIME ADSORPTION STUDIES ON Si(100)

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ABSTRACT

Adsorption of $SiClH_3$ and $SiCl_2H_2$ on Si(100) is studied as a function of surface temperature, comparing these precursors for Si Atomic Layer Epitaxy (ALE). At 450-550°C, a substantial surface H coverage (θ_H) exists during $SiClH_3$ adsorption, and θ_H exhibits transient behavior. During $SiCl_2H_2$ adsorption, θ_H is much smaller. At 500°C with $SiCl_2H_2$, $\simeq 1$ monolayer of Cl is formed after $\simeq 4 \times 10^{19}$ cm^{-2} exposure. Dichlorosilane is a suitable precursor for Si ALE, but desorption of HCl is significant at T > 500°C so that $SiCl_2H_2$ adsorption is not strictly self-limiting.

The epitaxial growth of II-VI and III-V semiconductor films in a self-limiting, layer-by-layer manner is called Atomic Layer Epitaxy (ALE) {1,2}. The number of ALE cycles directly determines the film thickness. Recent studies have explored the film growth {3,4} and surface chemistry {5-7} aspects of Si ALE from chlorosilanes. A hypothetical Si ALE cycle would consist of two steps : chlorosilane adsorption, and removal of surface Cl. Removal of Cl from the Si(100) surface using atomic hydrogen {8,9} at a surface temperature (T_S) where H_2 desorption occurs should allow dangling bond (db) regeneration. The optimum precursor for Si ALE will exhibit self-limiting adsorption at a useful growth temperature ($\simeq$ 500ºC). The Si coverage deposited per cycle is a secondary issue, because the present evidence indicates that no stable molecular precursor will deposit one full monolayer (ML) of Si per cycle {2,4,6}.

A problem with SiH_xCl_{4-x} precursors for Si ALE is that the adsorption T_S must be sufficiently high that H_2 desorbs rapidly from the surface, leaving the surface Cl terminated. Hypothetically, if all H atoms desorb as H_2 leaving 1 ML of Cl on the surface, the precursors $SiClH_3$ and $SiCl_2H_2$ might deliver $\simeq$1 ML and $\simeq$1/2 ML of new Si, respectively. Here, we study the chlorosilane adsorption step in real time. We demonstrate that adsorption is *only* self-limiting in the limit of T_S < 450ºC, when no desorption of adsorbed species occurs. At T_S sufficient for H_2 desorption ($\simeq$ 500ºC), HCl desorption also occurs so that db are replenished and chlorosilane adsorption is not self-limiting.

Time-of-flight Scattering and Recoiling Spectroscopy (TOF-SARS) {10} is used *in situ* to monitor the surface coverages of H and Cl as the gases are adsorbed {11}. The 4 keV K^+ beam is 9.5º from the surface plane and the recoiled (DR) particles are collected at the recoil angle Φ = 30º from the incident beam. Scattered K^+ ions are largely removed by a grid biassed at + 4 KV in front of the detector, and peak heights are used to measure coverage {11}. Dichlorosilane was purchased from Matheson and purified

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to > 99%, and SiClH₃ was synthesized by reaction of ISiH₃ with silver chloride and purified to 98% ($\simeq$ 2% $SiCl_2H_2$). Details will be described elsewhere {12}.

The DR spectra from static surfaces appear in Figure 1, with a clean Si(100) surface giving spectrum 1A. The Si direct recoil (Si_{DR}) flight time is 7.0 μs, with a shoulder at $\simeq$ 7.5-9 μs due to neutralized K^+. Spectrum 1B shows a 1 ML coverage of H (from atomic H at 425°C), and 1E shows $\simeq$1 ML Cl coverage (saturation from Si_2Cl_6 at 450°C). The H_{DR} and Cl_{DR} TOF's are 4.17 μs and 7.8 μs, respectively. These spectra are used to calibrate the H and Cl coverages from chlorosilanes. Spectra 1C and 1D are taken following saturation exposure to $SiClH_3$ and $SiCl_2H_2$, respectively, at 200°C. Note that the saturation coverages of $SiClH_3$ and $SiCl_2H_2$ at 200°C contain 1:3 and 1:1 ratios of Cl to H, respectively.

Figure 2 illustrates real time measurement of the Si(100) surface composition during adsorption at T_S =450°C in a flux of $\simeq$ 2×10^{17} $cm^{-2}s^{-1}$ of $SiClH_3$ (left) and $SiCl_2H_2$ (right). The adsorbed coverages of H and Cl show a pronounced dynamical behaviour. A *transient* H coverage is clearly seen with $SiClH_3$, where initially, the H_{DR} signal is large, but then *decreases* as hydrogen desorbs and more $SiClH_3$ adsorbs. This is also observed in $SiCl_2H_2$ adsorption, but to a lesser extent. The H_{DR} and Cl_{DR} signals reach steady state, but only after $\simeq$ 6-8 minutes at this flux. Chemisorbed chlorosilanes provide both H and Cl atoms to the surface adlayer. These data demonstrate thermodynamic control over the composition of this adlayer at T_S as low as 450°C. The Si-Cl bond energy is 4.2 eV and the Si-H monohydride bond energy is 3.3 eV, using gas phase thermochemical bond energies {13}. Kinetic barriers control the adlayer composition only at lower T_S (see Figure 1). Hydrogen and Cl coverages are calculated assigning the peak height in spectrum 1B to 1.0 ML of H, and using the relation θ_H + θ_{Cl} = 1.0. At steady state at T_S =450°C, we estimate Θ_{Cl} $\simeq$ 0.7 and Θ_H $\simeq$ 0.3 for

SiClH$_3$, and $\Theta_{Cl} \simeq 0.85$ and $\Theta_H \simeq 0.15$ for SiCl$_2$H$_2$. At $T_S = 450^\circ$C, no desorption of Cl is observed with the gas flux off for either molecule.

Dynamic adsorption of these gases was also studied at $T_S = 500^\circ$C, as shown in Figure 3. At this T_S, steady state is reached after $\simeq$ 2-3 minutes. The H$_{DR}$ signal from SiClH$_3$ (3A) is roughly constant, and with SiCl$_2$H$_2$ the H$_{DR}$ signal (3B) shows a transient behavior as in Figure 2. After $\simeq$ 3 min., $\Theta_{Cl} \simeq 0.75$ using SiClH$_3$ and $\Theta_{Cl} \simeq 1$ using SiCl$_2$H$_2$ at 500°C. To check for self-terminated adsorption, data acquisition was continued with the flux off. Both the H$_{DR}$ and Cl$_{DR}$ signal decrease in the SiClH$_3$ experiment (3A), while in the SiCl$_2$H$_2$ case (3B), the Cl$_{DR}$ signal remains constant. This experiment demonstrates that significant HCl desorption occurs on the timescale of 100 s at 500°C, therefore achieving $\Theta_{Cl} = 1$ and $\Theta_H = 0$ is necessary to prevent HCl desorption.

The DR spectra in Figure 4 under steady state conditions for SiClH$_3$ and SiCl$_2$H$_2$ at $T_S = 550^\circ$C look similar to Figure 3. Using SiCl$_2$H$_2$, $\Theta_{Cl} \simeq 1$ is achieved after 2-3 minutes at both 550 and 500°C. With the flux off, the Cl$_{DR}$ signal drops rapidly on the SiClH$_3$ dosed surface (4A), which is a consequence of the increased HCl desorption rate at 550°C. The small decrease in the Cl$_{DR}$ signal from SiCl$_2$H$_2$ is attributed to SiCl$_2$ desorption, because $\theta_H \simeq 0$. Desorption of SiCl$_2$ results in a net loss of Si from the surface, and guarantees that adsorption of any chlorosilane does not self-terminate.

The dynamic adsorption of SiClH$_3$ and SiCl$_2$H$_2$ at $T_S \simeq 450\text{-}550^\circ$C has implications for Si ALE. Using SiClH$_3$, a self-limiting Cl layer never forms, so SiClH$_3$ is not useful in Si ALE. Roughly 1 ML of Cl is formed using SiCl$_2$H$_2$ at $T_S = 500\text{-}550^\circ$C. At 550°C, desorption of SiCl$_2$ is observed on the 100 s timescale. With SiCl$_2$H$_2$, the optimum ALE temperature is 500°C. We detect HCl desorption at $T_S \geq 500^\circ$C, so that SiCl$_2$H$_2$ (or SiClH$_3$) adsorption is not strictly self-limiting at 500°C. During adsorption

a small amout of *continuous* Si growth occurs, and the amount depends on the flux and timescale of adsorption. Fully chlorinated silanes ($SiCl_4$ or Si_2Cl_6) eliminate many of the complications due to HCl desorption.

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FIGURE CAPTIONS

FIGURE 1.

TOF spectra from a clean Si(100)-(2X1) surface, and this surface saturated with different gases. The K^+ beam energy is 4 keV, with an incident angle, α, of 9.5°. Each spectrum was counted for 1 minute, with a K^+ beam current of $\simeq$ 0.04 nA. A: Clean Si(100). The Si_{DR} signal occurs at a TOF of 7.0 μs. B: Atomic H terminated surface dosed at 425°C. This corresponds to 1 ML of H on the Si(100) surface. C: $SiClH_3$ saturation dose at 200°C. D: $SiCl_2H_2$ saturation dose at 200°C. E: Si_2Cl_6 saturation dose at 425°C. This should correspond to 1 ML of Cl on the Si(100) surface {7}.

FIGURE 2.

DR spectra measured during dosing with $\simeq 2\times10^{17}$ cm^{-2}s^{-1} of A:$SiClH_3$ and B:$SiCl_2H_2$ at 450°C. The spectra were signal averaged for 1 minute each, and the time indicated in the figure is the end of the averaging period, so that 1 Min. corresponds to averaging from 0 to 1 Min.. Also shown in the upper right hand side of 2A is the height of the H_{DR} signal corresponding to $\Theta_H = 1$.

FIGURE 3.

Same as Figure 2, except that the surface temperature is 500°C, and the top spectra were acquired after the flux was turned off, beginning at 1 Min. and ending at 2 min..

FIGURE 4.

Same as Figure 3, except that the surface temperature is 550°C.

Fig. 1

Fig. 2

A: SiClH₃
T=450°C   θ_H=1

10 MIN.

3 MIN.

1 MIN.

GAS ON ↑

x 0.5

0 MIN.

4.17   7.0
Time Of Flight (μs)

B: SiCl₂H₂
T=450°C

10 MIN.

3 MIN.

1 MIN.

GAS ON ↑

x 0.5

0 MIN.

4.17   7.8
Time Of Flight (μs)

Recoil Intensity, Arb. Units

Fig. 3

Fig. 4

A: SiClH$_3$
T=550°C
$\theta_H=1$

2 MIN.

GAS OFF ↑

3 MIN.

1 MIN.

GAS ON ↑

× 0.5

0 MIN.

4.17   7.0
Time Of Flight (μs)

B: SiCl$_2$H$_2$
T=550°C

2 MIN.

GAS OFF ↑

3 MIN.

1 MIN.

GAS ON ↑

× 0.5

0 MIN.

4.17   7.8
Time Of Flight (μs)

Recoil Intensity , Arb. Units
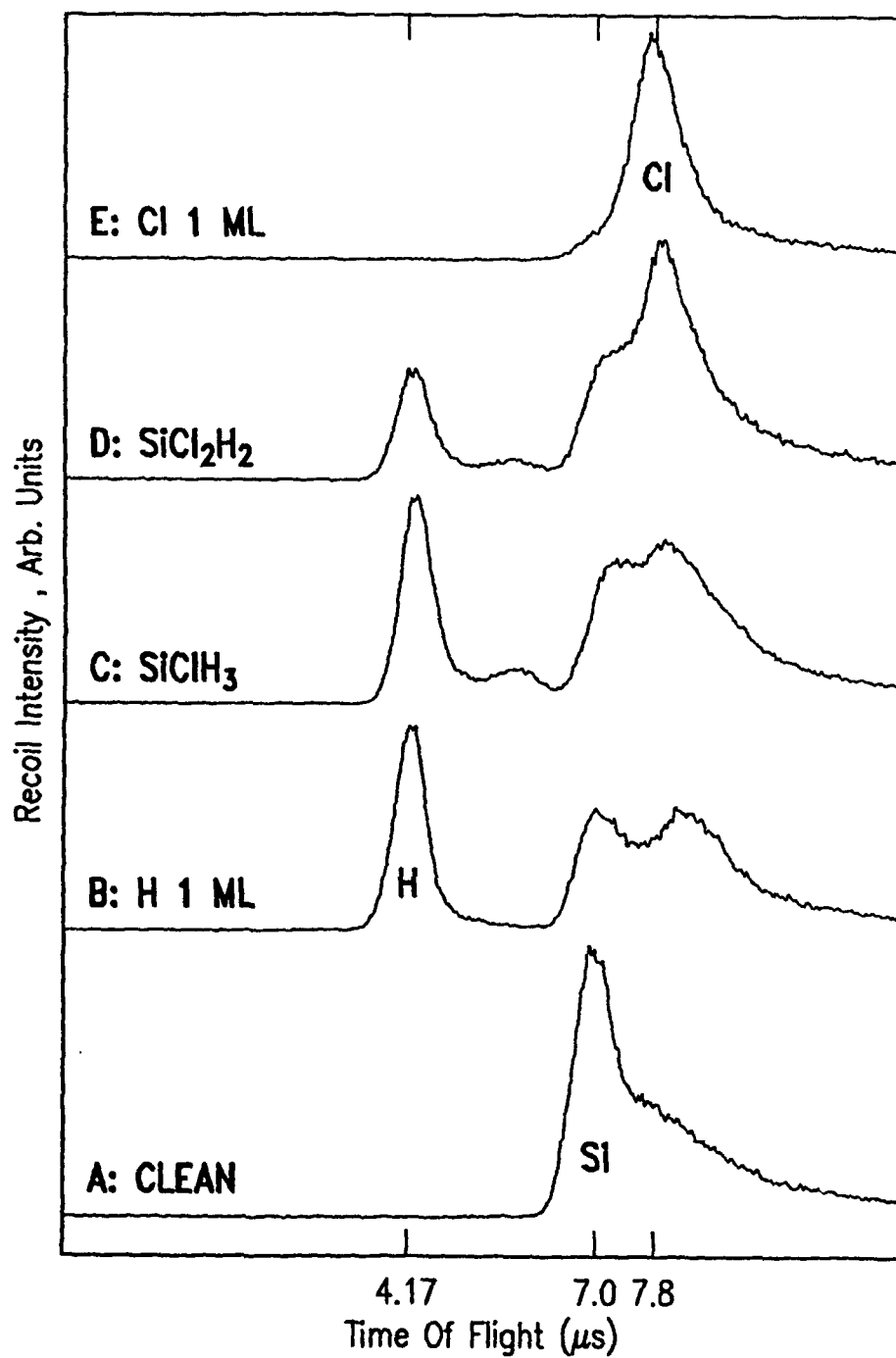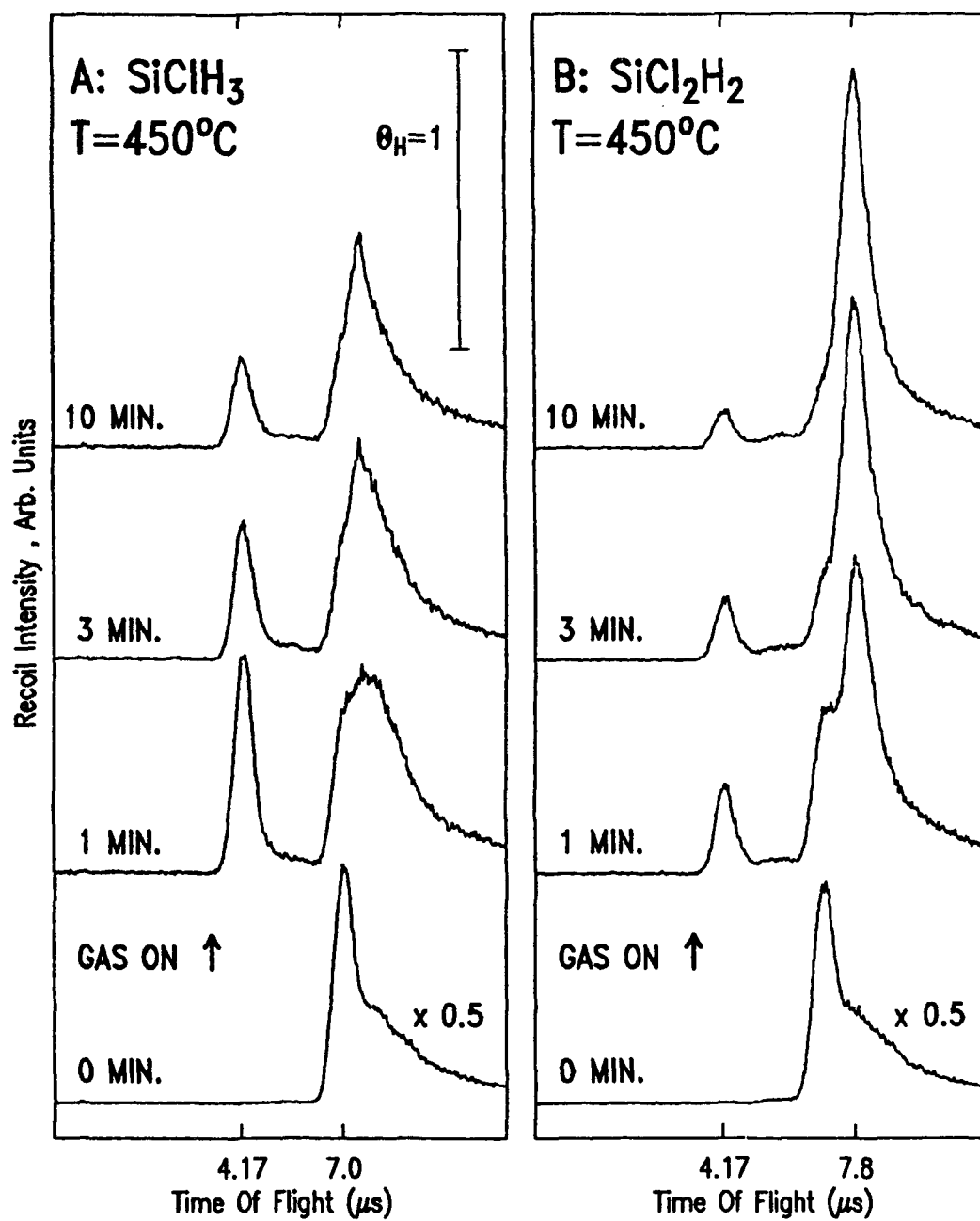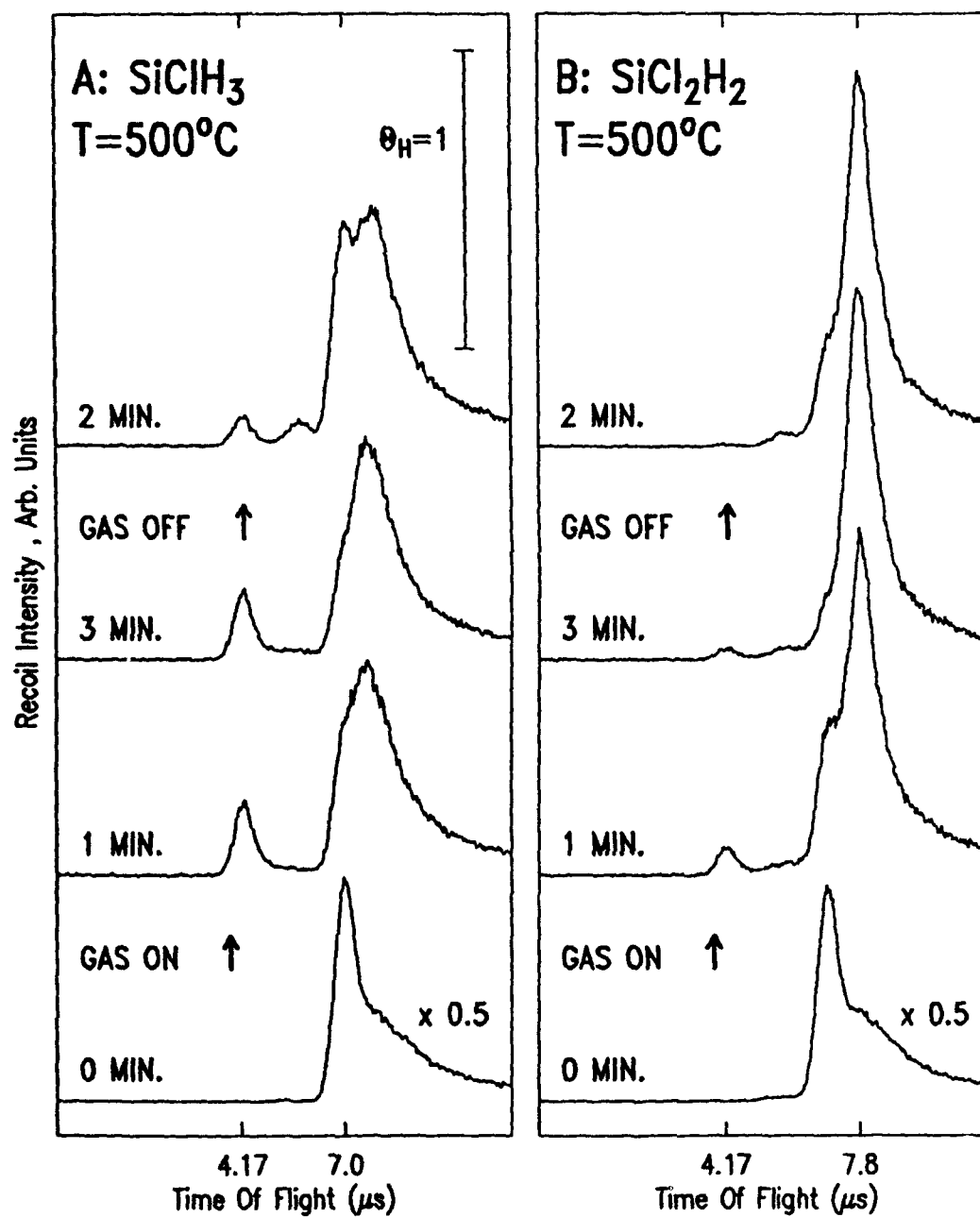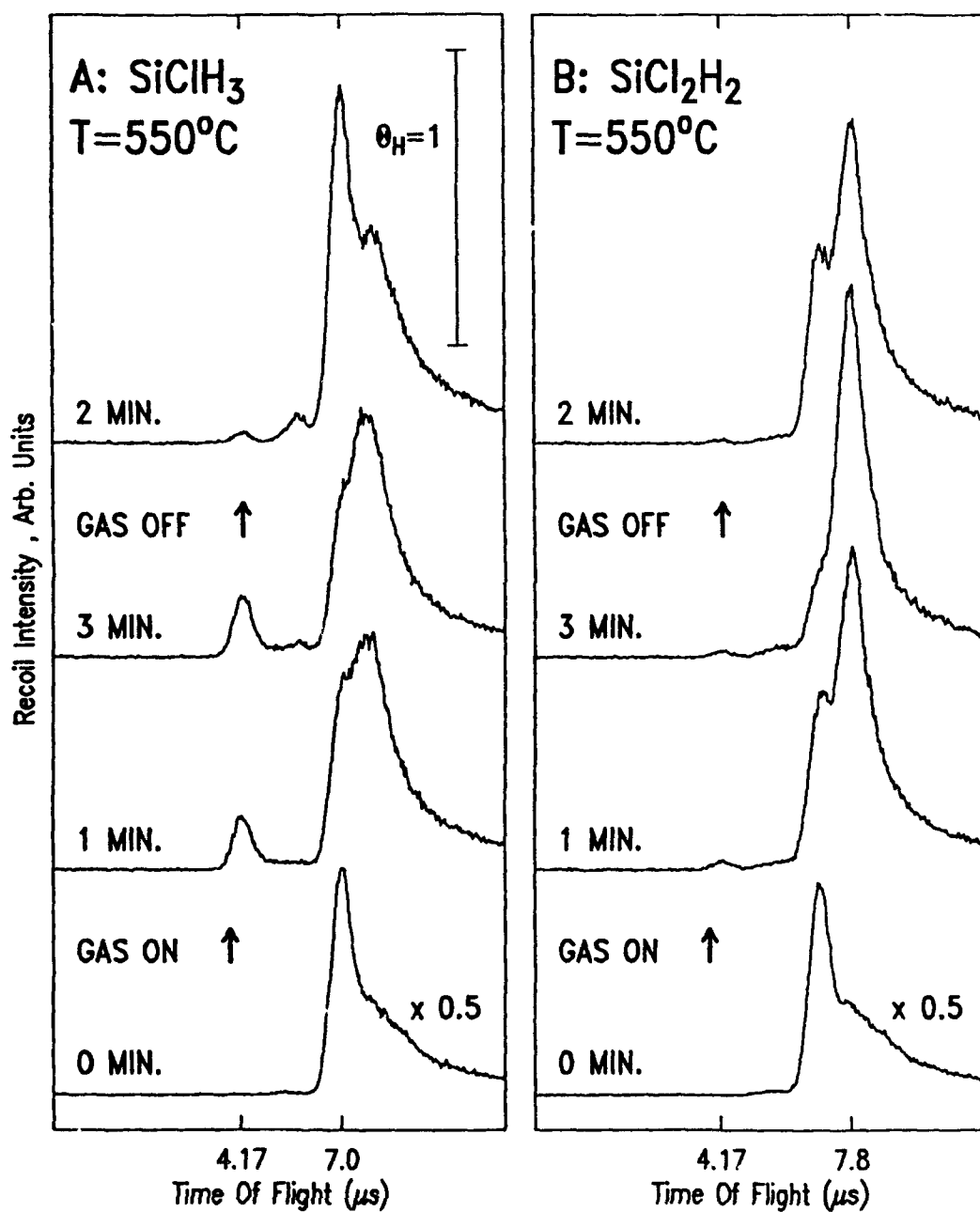
Comparison Of Chemical Schemes

For Si Atomic Layer Epitaxy

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ABSTRACT

Chemical schemes for Si Atomic Layer Epitaxy (ALE) are discussed using a 2-step sequence of reactions : 1. surface chlorination , using a chlorosilane molecule, and 2. reduction (Cl removal) using atomic H or a silane molecule. The schemes are compared in terms of equilibrium thermodynamics, to select the most promising schemes. All of the proposed processes based on atomic H are spontaneous (thermodynamically down-hill). Two reactions using Si_2H_6 are endothermic, but may be thermally driven at useful Si growth temperatures, due to a large, positive entropy change for the reaction.

I. Introduction

Thin film growth using cycles of self-limiting adsorption steps, with resulting layer-by-layer growth, is known as Atomic Layer Epitaxy (ALE) [1,2]. Extension of ALE from binary materials to elemental semiconductors such as Si or diamond is a research area of current interest. Concerning Si growth, motivations to develop this method are fine control over deposited film thickness, insensitivity of growth rate to changes in processing parameters, and the goal of depositing very abrupt "delta-doped" layers. Uniform growth rate over large areas is another useful feature of ALE. The possibility of layer-by-layer growth of single element materials , such as Si and diamond, is also a fascinating challenge which is stimulating research in the surface chemistry of these materials. The only previous example of Si film growth by ALE used self-limiting adsorption of Si_2H_6 at temperatures (T) below the H_2 desorption T, and rapid photothermal heating with an excimer laser pulse to desorb the surface hydrogen[3]. It is not clear what chemical schemes will be most useful for *isothermal* Si ALE at low temperature.

First, we examine thermodynamics of example reactions from the ALE literature on the growth of binary materials. These example ALE schemes use reactions that are "downhill" thermodynamically (negative ΔG). Second, potential schemes for Si ALE using chlorosilanes and H/Cl exchange chemistry[4,5] are compared with respect to equilibrium thermodynamics. Equilibrium is not reached in film growth reactors, but the hypothetical equilibrium case serves as a qualitative guide in choosing facile reactions that are "downhill" thermodynamically. Also, a closed reactor for investigating ALE chemistries with the reactants and film allowed to reach equilibrium in each cycle has been recently discussed[6]. Finally, Si reactions that are promising based on thermodynamics are discussed with regard to other factors.

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II. Thermodynamics Of ALE Schemes

A. Tables Of Thermodynamic Data

Tables I - IV summarize the equilibrium thermodynamics of the net reactions considered for ALE. The state labels are omitted from the reactions in all the Tables, for simplicity. All reactants, and H_2 and HCl products, are gases. The remaining products are solids. Tabulations of standard thermodynamic functions[7-9] were used to calculate ΔH^o and ΔG^o, both at 300 K. Also, ΔS^o was calculated (not shown) and an estimate of ΔG at 775 K (Est. ΔG) was made *assuming* that ΔH is independant of T, using Est. $\Delta G = \Delta H^o - (775 \text{ K} \times \Delta S^o)$.

B. ALE of ZnS, Ta_2O_5, Al_2O_3 and GaAs

Thermodynamics of four example reactions from the literature for the ALE growth of binary materials have been analyzed, with the results summarized in Table I. Literature references given in the table describe the use of these in ALE studies. Three examples use a metal halide reaction with either H_2S or H_2O[10]. The products are HCl gas and the metal sulphide or oxide. The last example is GaAs growth[11-14], and is more complicated. The growth of ZnS from H_2S and $ZnCl_2$ gases[10] is one of the most successful ALE processes[1,2] and is used industrially to make electroluminescent displays. Addition of different metal ion dopants to ZnS is used to produce different colors of electroluminescence[1,2].

All 4 example reactions in Table I are exothermic. The standard enthalpy changes (ΔH^o) at 300 K are all negative. These successful ALE schemes use the formation of

strong bonds in both the solid and gas products to drive the reaction. Also, for all these reactions ΔS is sufficiently small that ΔG remains negative below T = 800 K.

The ZnS formation reaction is characterized by a substantial negative entropy change (ΔS), and the Gibbs free energy change (ΔG) is therefore sensitive to T. While ΔG is negative at low T, it becomes positive at sufficiently high T. Lower reaction temperatures should favor this reaction, provided the T is sufficient to overcome the kinetic barriers to HCl desorption and lattice ordering.

The Ta_2O_5 and Al_2O_3 growth reactions are very similar in thermodynamics. Both are quite exothermic, and both have ΔS approximately equal to zero. At all useful oxide growth temperatures, ΔG is negative and large in magnitude for both reactions.

Several schemes for GaAs ALE have been reported[11-14]. The GaCl reaction was selected because tabulated data for GaCl are readily available, in contrast to GaR_3 where R = methyl, or ethyl. A furnace at 1050 K was used to produce GaCl in one case[12], and in the use of $GaCl(ethyl)_2$ gas phase pyrolysis is proposed to result in GaCl formation, with GaCl being the adsorbing Ga species[13]. The GaCl$\rightarrow$GaAs reaction is similar to the ZnS reaction in Table I, in that both reactions have negative ΔH^o and negative ΔS. Compared to the ZnS reaction, ΔS is smaller in magnitude for the GaCl$\rightarrow$GaAs reaction. Hence, the T dependance of ΔG is smaller for GaAs growth using GaCl, compared to the ZnS reaction.

C. $SiCl_2H_2$ Reactions For Si ALE

Dichlorosilane is widely used for the epitaxial growth of Si in chemical vapor deposition (CVD) reactors at total pressures in the range 1-760 torr. It is cheap and readily available. Useful fundamental information is available regarding thermodynamic data

[15], Si surface reactions[16,17] and ALE film growth[18,19] with $SiCl_2H_2$. We use $SiCl_2H_2$ as a typical chlorosilane to illustrate the general pattern of 2 reaction steps for all of the Si ALE schemes considered here. This pattern is shown schematically in Figure 1. The chlorination step consists of exposing the clean Si surface to a chlorosilane ($SiCl_2H_2$, for example) at $T \simeq 775$ K (500°C). The balanced stoichiometric reactions shown in Tables II-IV consider all hydrogen atoms in the chlorosilane (marked H') desorbing from the surface as dihydrogen (H'_2) in the chlorination step. On the clean Si(100) surface, thermal desorption of 1/2 ML of H as H_2 requires $\simeq 200$ s at 775 K[20]. The result is a Si surface terminated with Cl. This surface is stable (free of measurable Cl desorption) in vacuum for several hundred seconds at 775 K[16,21]. Ideally, 1 ML of Cl should be formed in the chlorination step to ensure that a self-limiting layer with a maximum amount of Si is adsorbed. If H remains co-adsorbed with Cl, HCl desorption will occur. Recently, our experiments have suggested $SiCl_2H_2$ and $SiClH_3$ do not adsorb at 775 K exactly as depicted, because some HCl desorption occurs during the chlorination step[21]. The fully chlorinated molecules $SiCl_4$ and Si_2Cl_6 should behave exactly as depicted in Figure 1, both forming 1 ML of surface monochloride. A formal scheme is necessary, in order to write stoichiometric equations and compare the molecules we wish to consider.

The reduction step consists of using a reducing agent to remove the Cl adlayer. Both silanes and atomic hydrogen (H) are compared here for use as this reducing agent. The stoichiometric coefficient of the reducing agent is selected to convert all Cl atoms in the chlorosilane to HCl in the reduction step. At 775 K, the rate of HCl desorption is $\simeq 20$ times that of $SiCl_2$ desorption[16]. The upper limit of T for a stable Cl layer is $<$ 825 K. At this T, significant $SiCl_2$ desorption occurs[21] in $\simeq 100$ s.

Table II compares the thermodynamics of 4 potential Si ALE schemes using $SiCl_2H_2$, with 3 silanes and atomic H considered as the reducing agent. Tabulated data for Si_3H_8 do not allow calculation of ΔS or ΔG for reaction with Si_3H_8. It is seen that the reactions of $SiCl_2H_2$ with silanes are all endothermic, (ΔH^o positive) and ΔH^o increases in magnitude upon going from SiH_4 to Si_2H_6 to Si_3H_8. This is because the higher the silane, more $SiCl_2H_2$ molecules are used to make net reactions that are stoichiometrically balanced (with respect to H atoms in the silane, Cl in $SiCl_2H_2$, and product HCl). More $SiCl_2H_2$ molecules means more Si-Cl bonds in the reactants, and it is the Si-Cl bonds that dominate when estimates of ΔH are made using bond energies.

In order to discuss the entropy changes, we note that the $SiCl_2H_2$ reactions with silanes all produce net molecules of gas. As the reducing agent goes from SiH_4 to Si_2H_6 to Si_3H_8, the net number of gas molecules produced increases from 3 to 5 to 7. These reactions therefore have relatively large, positive, entropy changes, and ΔS increases from SiH_4 to Si_3H_8. Therefore, the magnitude and sign of ΔG have a strong temperature (T) dependance. The $SiCl_2H_2$ reactions with silanes are "uphill" (ΔG positive) at low T (300 K), but become "downhill" (ΔG negative) at useful film growth temperatures.

In contrast to reaction with the silanes, the $SiCl_2H_2$ plus atomic H reaction is exothermic, and ΔG is not T sensitive. Zero net gas molecules are produced, so $\Delta S \simeq 0$ (1.6 cal/K mole). The $SiCl_2H_2$ + atomic H reaction is driven by the exothemic formation of HCl, H-H and Si-Si bonds, is "downhill" at all temperatures that are useful for Si growth, and appears viable for Si ALE growth.

Two decomposition reactions of $SiCl_2H_2$ are also included at the bottom of Table II : reaction to Si plus 2 HCl, and formation of $SiCl_2$ plus H_2. Both reactions are

6

endothermic, and ΔS is small, so that entropy does not help make these reactions "downhill" unless T > roughly 1200 K. The dichlorosilylene formation reaction has a slightly larger ΔS^o than the HCl formation reaction. Dichlorosilylene formation has a negative ΔG above 1192 K, while HCl formation has a negative ΔG above 1217 K. Note that adding 1 molecule of H_2 to both the reactants and the products of the $SiCl_2H_2$ reactions does not change the thermodynamics. A Si ALE process operating at high T (1100-1200 K) using $SiCl_2H_2$ and H_2 has been reported by Nishizawa and co-workers[19]. The reaction shown in Table II as $SiCl_2H_2 \rightarrow Si + 2\ HCl$ is stoichiometrically equal to the same reaction with H_2 added to both sides, so the $SiCl_2H_2 \rightarrow Si + 2\ HCl$ reaction in Table II gives a rough approximation of the thermodynamics of the Nishizawa process. The role of H_2 is probably to inhibit $SiCl_2$ formation (which removes Si, not depositing Si), by providing surface H to enhance the desorption rate of HCl.

D. Reactions of Chlorosilanes With Atomic Hydrogen

Table III compares the thermodynamics of ALE schemes based on atomic hydrogen (H) as the reducing agent, and using 4 different chlorosilane molecules (and the $SiCl_2$ radical). Referring to Figure 1, deposition of Si would only occur in the chlorination step of our reaction sequence, and Si deposition should be self-limiting due to saturation of the surface with 1 ML (or nearly 1 ML) of Cl. No further Si is deposited in the reduction step using atomic H, so the net reactions with atomic H are all self-limiting with respect to Si growth.

Published thermodynamic data do not permit ΔG or ΔS calculation for the Si_2Cl_6 reaction. All 5 reactions in Table III are exothermic. The more Cl atoms there are in the chlorosilane, the more negative is ΔH. Gas phase thermochemical bond energies are

useful to rationalize this. The Si-Cl bond energy is 96 Kcal/mole[22]. For each Si-Cl bond broken, both an H-Cl(gas) and a Si-Si(solid) bond are formed in the products, with bond energies of 103[22] and $\simeq 50$[23] Kcal/mole, respectively. The contribution to ΔH is roughly 50-60 Kcal/mole per Cl atom in the chlorosilane. Net molecules of gas produced lie in the range -1 to 1 for these reactions, so ΔS is small for all the reactions in Table III. The magnitude and sign of ΔG are therefore *insensitive* to T, allowing the optimum reaction T to be selected using kinetic considerations. Table III shows that there is no thermodynamic advantage to using both $SiCl_2$ and atomic H in an ALE scheme (compared to a stable molecule and atomic H), so $SiCl_2$ is considered below for use with Si_2H_6. All of the reactions in Table III are characterized by negative ΔG at the temperatures of interest for Si growth. All of these schemes look promising for Si ALE, and the optimum choice will not be made using thermodynamics.

E. Reactions of Chlorosilanes With Disilane, Si_2H_6

Table IV compares reaction thermodynamics for 5 Si ALE schemes using the same 5 chlorosilanes considered above, but with Si_2H_6 as the reducing agent. Referring to Figure 1, a disadvantage of using Si_2H_6 is that deposition of Si would occur in *both* chlorination and reduction steps, and Si deposition may not be self-limiting (see below). However, use of a stable molecule as reducing agent would eliminate the need to use a plasma or hot filament for dissociation of H_2 to H. Contamination of the growing Si film by trace H_2O, OH, hydrocarbon radicals, and other impurities may be a severe problem with atomic H ALE processes. Disilane has been selected as a prototype silane for several reasons. The data in Table II indicated that for reaction with $SiCl_2H_2$, comparing Si_2H_6 and SiH_4 as reducing agents, Si_2H_6 is more favorable thermodynamically at 775 K. Also, Si_2H_6 is $\simeq 10^3$ times more reactive on clean Si surfaces than SiH_4[24]. There are stability problems with Si_3H_8. Disilane is reactive, convenient and commercially available, and thus is the best choice.

Regarding the enthalpy changes reported in Table IV, reactions of Si_2H_6 with stable chlorosilane molecules are all endothermic (ΔH^o positive). Strong Si-Cl and Si-H bonds in the reactant are responsible. Only the reaction with $SiCl_2$ radical is exothermic. Regarding entropy changes, net molecules of gas are produced in all of the Si_2H_6 reactions, hence ΔS is positive for each reaction. For the cases of $SiCl_4$ and $SiClH_3$, the magnitude of ΔS is not sufficient for ΔG to be negative at useful temperatures. The positive ΔH^o term is too large. Using the data of Table IV to evaluate the use of Si_2H_6 as reducing agent, the chlorosilanes $SiCl_2H_2$ and $SiCl_2$ have ΔG negative at useful temperatures.

The $SiCl_2$ + Si_2H_6 reaction thermodynamically fits the pattern of proven ALE schemes, but production of $SiCl_2$ with a flux that is useful for film growth is an uncertain prospect. Proven ways to make this radical include photolysis of Si_2Cl_6[25], pyrolysis of higher perchloropolysilanes at T = 800 to 875 K [26], and infrared multiphoton dissociation of $SiCl_2H_2$ [27]. Pyrolysis of Si_2Cl_6 or $SiCl_4$ in a heated tube in close proximity to the growth surface might produce sufficient flux of $SiCl_2$ to be useful as an ALE precursor.

Consider now the 4 stable molecules compared in Table IV. The reactions of $SiCl_4$ and $SiClH_3$ both have ΔH^o greater than 100 Kcal/mole, and ΔG for these reactions remains positive at T = 775 K. These 2 reactions can be ruled out of further consideration for Si ALE. The reactions of Si_2Cl_6 and $SiCl_2H_2$ both have ΔH^o less than 80 Kcal/mole. In the $SiCl_2H_2$ case, the ($T\Delta S$) term has a strong effect on ΔG, and ΔG becomes negative at T $\simeq$ 775 K, a useful film growth T. The $SiCl_2H_2$ + Si_2H_6 reaction deserves further study to investigate the possibility of using entropy driven reactions in Si ALE.

A convoluted argument is now made in order to substantiate a simple point. The two chlorosilane molecules $SiCl_2H_2$ and Si_2Cl_6 should *both* be considered for potential use in entropy driven reactions for Si ALE using molecular precursors. As seen in Table IV, the Si_2H_6 reactions with $SiCl_2H_2$ and Si_2Cl_6 have similar $\Delta H^o = 75 \pm 2$ Kcal/mole. The $SiCl_2H_2$ reaction has a large ΔS (+ 113 cal/K mole), which makes ΔG negative at 775 K. Lacking published entropy data for Si_2Cl_6, we extrapolate from the $SiCl_2H_2$ reaction to the Si_2Cl_6 reaction, in order to estimate the magnitude of ΔS for the Si_2Cl_6 + Si_2H_6 reaction. The ratio of product gas molecules/reactant gas molecules in the stoichiometric equations is a gauge of ΔS. This ratio is 3 for Si_2Cl_6 + Si_2H_6, and is 2.5 for $SiCl_2H_2$ + Si_2H_6. Thus, in the Si_2Cl_6 case ΔS should be larger than 113 cal/K mole, and entropy should make the Si_2Cl_6 reaction downhill at some T even less than 775 K.

Using $SiCl_2H_2$ and Si_2H_6 the idealized scheme (Figure 1) would deposit 1/2 ML of Si per cycle in the chlorination step, and some amount of Si from Si_2H_6 during the reduction step. This amount of "extra" Si will depend on the process T, and is not simple to estimate. The T dependance of the Si grown per cycle using Si_2H_6 must be experimentally determined. The observed T dependance of the rate of H and Cl exchange using Si_2H_6 and Si_2Cl_6 is that exchange is more rapid the higher the T[5]. This is consistent with an entropy driven reaction, but is also consistent with an energetic barrier (such as the activation energy for HCl desorption) that is surmounted using thermal energy.

F. Summary of Comparative Thermodynamics

Using equilibrium thermodynamics, ALE reactions from the literature were compared, and a pattern of thermodynamically "downhill" reactions was established. For these examples, the reactions are enthalpy driven (exothermic) and ΔS is small, so ΔG is negative at film growth temperatures. Two classes of schemes for Si ALE were then

identified as having negative ΔG at $T \simeq 775$ K. One class of Si reactions with negative ΔG make use of either 1 or 2 radical reactants. These Si radical reactions are enthalpy driven, and *fit the pattern of proven ALE schemes*: negative ΔH^o, small ΔS, resulting negative ΔG, and ΔG weakly T dependant. Reactions of all chlorosilane molecules with atomic H, and reaction of $SiCl_2$ radical with Si_2H_6 are in the class of "radical" schemes for Si ALE. The dichlorosilylene radical, $SiCl_2$, is the optimum chlorosilane precursor, judging strictly by thermodynamics. However, production of a useful flux of this species may not be possible using known methods.

The second class of reactions consists specifically of two entropy driven reactions us-ing stable molecules. The reactions of either Si_2Cl_6 or $SiCl_2H_2$ with the reducing agent Si_2H_6 are endothermic, but a large, positive ΔS makes ΔG strongly T dependant. At sufficiently high T (but within the limits of useful film growth T), ΔG becomes negative. These Si growth reactions are not strictly self-limiting. However, practical consider-ations may dictate the selection of an optimum chemistry, so the $SiCl_2H_2 + Si_2H_6$ and $Si_2Cl_6 + Si_2H_6$ reactions deserve close scrutiny. A process chemistry using stable mol-ecules is desirable, so that Si_2H_6 as a reducing agent may be preferrable to atomic H.
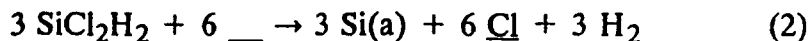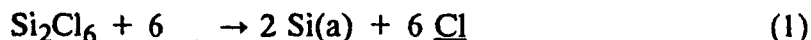
Equilibrium thermodynamics as summarized in Tables II-IV provides concrete evi-dence supporting 3 concepts to guide future studies in Si ALE chemistry.

1. Processes that are both truly self limiting *and* thermodynamically downhill will re-quire useful fluxes of free radicals (such as atomic H) that are free of contaminants.

2. To implement atomic H processes for Si ALE, the optimum choice of chlorosilane precursor is not dictated by energetics, because all of these are exothermic. Factors discussed below will dictate this choice.

3. Entropy driven ALE reactions using molecular reducing agents should be explored, and the limitations of this approach should be investigated.

III. Entropy Driven Si ALE Schemes

To understand the limitations of ALE reactions requiring thermal activation through the entropy term, we now examine features of the separate reaction steps (Figure 1), rather than the net reaction. The 2 separate steps shown in Figure 1 are Chlorination (adsorption of the chlorosilane precursor) and Reduction (Si_2H_6 reaction with the Cl-terminated surface to form HCl). We can explore the thermodynamics of the separate reactions using approximate methods.

One question is which precursor ($SiCl_2H_2$ or Si_2Cl_6) will be a better chlorosilane to use with Si_2H_6? The reduction steps are identical for both precursors. First, we consider the 2 adsorption reactions (chlorination steps), 1 and 2.

$$Si_2Cl_6 + 6 \underline{\quad} \rightarrow 2\, Si(a) + 6\, \underline{Cl} \qquad (1)$$

$$3\, SiCl_2H_2 + 6 \underline{\quad} \rightarrow 3\, Si(a) + 6\, \underline{Cl} + 3\, H_2 \qquad (2)$$

The symbol $\underline{\quad}$ represents a dangling bond on a surface Si atom, and $\underline{Cl}$ is a surface Si monochloride. The following are gas phase species : Si_2H_6, Si_2Cl_6, $SiCl_2H_2$, H_2, HCl. It is unclear how many bonds the adsorbed Si atoms (Si(a)) form. We assume 2 bonds per Si(a), and 54 Kcal/mole as the Si-Si bond energy[28]. With this assumption, and using tabulated gas phase bond energies[22,23], approximate enthalpy changes for these two chlorination steps are $\Delta E_1 = -162$ Kcal/mole and $\Delta E_2 = -181$ Kcal/mole. Both are substantially exothermic, but the estimated exothermicity is not accurate as it depends on the assumptions used about Si-Si bond formation. There is no reason to favoring either $SiCl_2H_2$ or Si_2Cl_6 based on thermodynamics.

The reduction step is reaction (3), and is the same for both Si_2Cl_6 and $SiCl_2H_2$.

$$6 \underline{Cl} + Si_2H_6 \rightarrow 2 \, Si(s) + 6 \, HCl + 6 \, \_ \qquad (3)$$
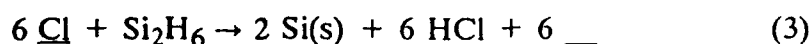
Published thermodynamic data allow us to probe ΔS for each step in the $SiCl_2H_2$ reaction (4), which is the sum of (2) and (3).

$$3 \, SiCl_2H_2' + Si_2H_6 \rightarrow 5 \, Si(s) + 3 \, H_2' + 6 \, HCl \qquad (4)$$

Table V contains estimates of the thermodynamics of the separate chlorination (2) and reduction (3) steps. (The lower 2 lines of Table V concerning the net reaction (4) are included to illustrate the accuracy of the entropy estimates, and the inaccuracy of the enthalpy estimates from bond energies.) It is clear that chlorination should be a trivial step to carry out, as we have shown that the adsorption of $SiCl_2H_2$ (or Si_2Cl_6) onto dangling bond terminated Si surfaces is quite exothermic. Adsorption of silanes occurs spontaneously at surface temperatures of 100 K when the surfaces are dangling bond terminated[28]. Also, ΔS for chlorination is negative but not large in magnitude.

It is the reduction step that is endothermic and requires moderately high temperatures to make the $(-T\Delta S)$ term larger than 73 Kcal/mole. Production of 5 moles of HCl per mole of Si_2H_6 reactant results in the large, positive ΔS for reaction (3) that makes this reaction "entropy driven".

IV. Practical Considerations For Si ALE

A. Selection Of Chlorosilane Precursor

We have just seen that $SiCl_2H_2$ and Si_2Cl_6 appear very similar as ALE precursors in terms of thermodynamics. Assuming the formation of 1 surface monochloride species from each Cl in the molecule, and termination of all Si dangling bonds with

monochloride, each of these molecules can react up to 1 ML Cl coverage in the chlorination step. Assuming this, and using atomic H (Table III), $SiCl_2H_2$ and Si_2Cl_6 will deposit 1/2 and 1/3 ML of Si per cycle, respectively. Given that 1/2 and 1/3 ML of Si are similar amounts, and both are significantly less than 1 ML, Si_2Cl_6 should be considered to be a useful precursor for Si ALE. Hexachlorodisilane has a high sticking probability[29] compared to 3×10^{-3} for $SiCl_2H_2$[16]. Also, Si_2Cl_6 is a low volatility liquid (vapor $P \simeq 5$ torr at 300 K) that is safer to handle than a combustible gas. The use of Si_2Cl_6 as a Si precursor has been demonstrated in CVD growth of SiO_2 and silicon oxynitride films[30]

One advantage of $SiCl_2H_2$ is that it is widely used for conventional Si chemical vapor deposition processes and is sold commercially in large quantities. We have found some evidence that HCl desorption *during the chlorination step* is a complicating factor with $SiCl_2H_2$[21]. Considering the chlorination reactions (1) and (2) shown above, reaction (1) should proceed to completion easily, and form 1 ML of Cl to self-terminate the reaction. On the other hand, reaction (2) assumes H_2 desorption as the only H removal path. At too low a surface T, H_2 desorption will be incomplete leaving H on the surface and incomplete Cl ML formation. At too high a surface T, HCl desorption will compete with H_2, and chlorination will not be self-terminating. This complication is eliminated with Si_2Cl_6.

B. Optimum Process Temperature

The general pattern shown in Figure 1 is assumed in this discussion. The maximum T (upper limit) that will allow truly self limiting growth using chlorosilanes is dictated by 2 factors. One factor is the time required to desorb a significant fraction of 1 ML of Cl from the surface. The second factor is the time required to adsorb 1 ML of Cl (to complete the chlorination step of Figure 1). Simple, but rigorous, estimates are made

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by considering the time to desorb 0.1 ML of Cl at various temperatures. We use desorption kinetics for $SiCl_2$[16], and a plot of $SiCl_2$ desorption rate vs. T for a Cl coverage of 0.16 ML [30], as reported by Coon, George and co-workers. We estimate that the order of magnitude time to desorb 0.1 ML of Cl as $SiCl_2$ is 0.1 s at 1075 K, 1 s at 975 K, 10 s at 925 K and 100 s at 875 K. The second factor, adsorption time, is dictated by 2 variables : chlorosilane flux, and adsorption kinetics (sticking probability). Reactor design may also be involved. If we assume a 1 s timescale to complete the chlorination step, this places a rigorous upper limit of $\simeq$ 975 K on the process T for Si ALE. Longer timescales for chlorination (adsorption) will call for lower temperature. The processing T used in Nishizawa's pioneering study was 1100-1125 K[19]. At this T, the desorption time for 0.1 ML of Cl would be < 0.1 s. All of the dosing or evacuation steps are 2-20 s in duration, so that this T precludes true self limiting Si ALE.

The lower T limit is more interesting to consider, due to the motivation to grow epitaxial Si at the lowest possible T, in order to prevent the decomposition of layered structures of disimilar materials during fabrication. It is the lower limit of processing T that may give atomic H processes (Table III) an advantage over the entropy driven Si_2H_6 processes discussed above. The chlorination steps (adsorption onto dangling bond terminated Si surfaces, such as reactions (1) and (2)) for all of these schemes are exothermic. This step has no high T requirement. The abstraction of Cl by atomic H exhibits a very small activation energy ($\simeq$ 2 Kcal/mole)[4], and proceeds readily at 300-600 K, so this step has no high T requirement. Thermal desorption of H from the Si surface is an implicit aspect of the atomic H schemes (to regenerate a dangling bond terminated surface), and this places a lower limit of 750 $\pm$ 25 K on the reaction T. For the entropy driven schemes, reduction with Si_2H_6 as shown in reaction (3) also requires T at least $\simeq$ 750 K for the reaction to proceed[5]. Atomic H and Si_2H_6 based reactions appear about the same in terms of the minimum T required.

V. Summary

The chemical reaction schemes from the ALE literature examined in Table I are all characterized by being exothermic, and by having ΔG negative at film growth temperatures of 700 ± 100 K. It is concluded that a thermodynamically "downhill" reaction scheme is required for successful ALE. Analysis of the thermodynamics of several potential schemes for Si ALE has lead to the following conclusions.

1. The reactions of $SiCl_2H_2$ + Si_2H_6 and Si_2Cl_6 + Si_2H_6 are not exothermic, but may be entropy driven at useful film growth temperatures. These reactions with Si_2H_6 as reducing agent should be attempted at high T ($\simeq$ 775 to 800 K) to maximize the entropy driven ($T\Delta S$) effect.

2. These schemes are *not* self-limiting with respect to Si deposition, but process conditions can be selected so the amount of Si grown/cycle can be well calibrated.

3. Truly self-limiting schemes for Si ALE based on the radical atomic H are enthalpy driven, and fit the pattern of examples from the ALE literature.

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Table I : Example ALE Reactions From Literature

REACTION	ΔH° at 300 K, Kcal/mole	ΔG° at 300 K, Kcal/mole	Est. ΔG at 770 K, Kcal/mole	Comment
$ZnCl_2 + H_2S \rightarrow ZnS + 2\ HCl$	-24.9	-16.3	-2.7	Refs. 1,2,10 Note (a)
$2\ TaCl_5 + 5\ H_2O \rightarrow Ta_2O_5 + 10\ HCl$	-58	-59	-60	Refs. 2, 10 Note (a)
$2\ AlCl_3 + 3\ H_2O \rightarrow Al_2O_3 + 6\ HCl$	-75.6	-74.0	-71.6	Ref. 2 Note (a)
$GaCl + AsH_3 \rightarrow GaAs + H_2 + HCl$	-35.8	-30.0	-20.9	Refs. 12,13

(a) Thermodynamic data from refs. 7,8.

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Table II : $SiCl_2H_2$ Reactions[a]

REACTION	$\Delta H°$ at 300 K, Kcal/mole	$\Delta G°$ at 300 K, Kcal/mole	Est. ΔG at 775 K, Kcal/mole
$2\ SiCl_2H_2' + SiH_4 \rightarrow 3\ Si + 2\ H'_2 + 4\ HCl$	+ 53.4	+ 33.1	+0.2
$3\ SiCl_2H_2' + Si_2H_6 \rightarrow 5\ Si + 3\ H'_2 + 6\ HCl$	+ 73.2	+ 39.7	-14.6
$4\ SiCl_2H_2' + Si_3H_8 \rightarrow 7\ Si + 4\ H'_2 + 8\ HCl$	+94.3	--	--
$SiCl_2H_2' + 2\ H\bullet \rightarrow Si + H'_2 + 2\ HCl$	- 73.4	-73.8	-74.6
$SiCl_2H_2 \rightarrow Si + 2\ HCl$	+ 30.8	+ 23.3	+ 11.3
$SiCl_2H_2 \rightarrow SiCl_2 + H_2$	+ 35.4	+ 26.6	+ 12.5

(a) $SiCl_2H_2$ thermodynamic data from ref. 15.

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Table III : Self-Limiting Reactions with H•

REACTION	ΔH^o at 300 K, Kcal/mole	ΔG^o at 300 K, Kcal/mole	Est. ΔG at 775 K, Kcal/mole	Comment
$Si_2Cl_6 + 6\ H\bullet \rightarrow 2\ Si + 6\ HCl$	-216.3	--	--	Note (a)
$SiCl_4 + 4\ H\bullet \rightarrow Si + 4\ HCl$	-138.4	-136.6	-134.1	
$SiCl_2H'_2 + 2\ H\bullet \rightarrow Si + H'_2 + 2\ HCl$	-73.4	-73.8	-74.6	Note (b)
$SiClH_3' + H\bullet \rightarrow Si + 3/2\ H'_2 + HCl$	-25	-28	-32	
$:SiCl_2 + 2\ H\bullet \rightarrow Si + 2\ HCl$	-108.8	-100.4	-87.9	

(a) Si_2Cl_6 ΔH^o of formation from ref. 32.

(b) $SiCl_2H_2$ thermodynamic data from ref. 15.

Table IV : Non-Self-Limiting Reactions With Si_2H_6

REACTION	$\Delta H°$ at 300 K, Kcal/mole	$\Delta G°$ at 300 K, Kcal/mole	Est. ΔG at 775 K, Kcal/mole	Comment
$Si_2Cl_6 + Si_2H_6 \rightarrow 4\ Si + 6\ HCl$	+77	--	--	Note a.
$3\ SiCl_4 + 2\ Si_2H_6 \rightarrow 7\ Si + 12\ HCl$	+171.6	+112.2	+31.6	
$3\ SiCl_2H_2' + Si_2H_6 \rightarrow 5\ Si + 3\ H'_2 + 6\ HCl$	+73.2	+39.7	-14.6	Note b.
$6\ SiClH_3' + Si_2H_6 \rightarrow 8\ Si + 9\ H'_2 + 6\ HCl$	+136	+91	+24	
$3\ :SiCl_2 + Si_2H_6 \rightarrow 5\ Si + 6\ HCl$	-33.0	-40.0	-50.0	

(a) Si_2Cl_6 $\Delta H°$ of formation from ref. 32.

(b) $SiCl_2H_2$ thermodynamic data from ref. 15.

Table V : Approximate Thermodynamics Of Chlorination And Reduction Steps of The $Si_2H_6 + SiCl_2H_2$ Reaction

REACTION	ΔE (a) Kcal/mole	Est. ΔS° (b) cal/K mole	Est. ΔG at 300 K, Kcal/mole	Est. ΔG at 775 K, Kcal/mole
(2) Chlorination	- 181	- 50	- 196	- 220
(3) Reduction	+ 272	+ 163	+ 223	+ 145
(4) Net Reaction, These Approximations	+ 91	+ 113	+ 57	+ 3
(4) Net Reaction, From Table IV	+ 73.2	+ 113.3	+ 39.7	- 14.6

(a) Estimated ΔH using Bond Energies (D) From Refs. 22, 23 and 28, and the assumption that D(Si-Cl) in $SiCl_2H_2$ = D(Si-Cl) in surface monochloride, Cl.

(b) Estimated using ΔS° from literature, and an approximate ΔS° for surface monochloride, Cl 33.

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FIGURE CAPTION

FIGURE 1.   Schematic representation of the formal scheme used in Tables II, III, IV, and V, and throughout the text, for Si Atomic Layer Epitaxy. Each growth cycle consists of 1 chlorination and 1 reduction step.

Fig. 1